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(54) **Planographic printing plate precursor**

(57) A positive planographic printing plate which has high sensitivity, limited reduction in sensitivity over time and high stability over time. The positive planographic printing plate has a light-sensitive layer formed on a support. The light-sensitive layer includes a light-sensitive image-forming material and a material which absorbs

light and generates heat. The light-sensitive image-forming material contains a novolac resin having a xylenol monomer. It is preferable that, if a proportion of the xylenol-containing novolac resin in alkali-soluble resin that forms the light-sensitive layer is Y% by weight and a content of the xylenol monomer in the novolac resin is X% by weight, $X \times Y$ is 500 or more ($X \times Y \geq 500$).

EP 1 162 063 A2

Description

BACKGROUND OF THE INVENTION

5 Field of the Invention

[0001] The present invention relates to a positive planographic printing master plate which may be used as an offset printing master, and particularly to a positive planographic printing master plate for so-called direct plate-making which enables plate-making directly from digital signals of a computer or the like.

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Description of the Related Art

[0002] Significant progress has been made with lasers in recent years. Of solid lasers and semiconductor lasers having a light emission region from the near infrared region to the infrared region, those having high output power and a small size have come to be easily available. These lasers are very useful as light sources for exposure in plate-making directly from digital data of computers and the like.

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[0003] In positive light-sensitive image forming materials for infrared lasers used for conventionally known direct plate-making, a novolac resin is used as a resin soluble in an aqueous alkali solution. For example, a positive light-sensitive image-forming material disclosed in JP-A No. 7-285275 is produced by adding a material which absorbs light to generate heat and a positive light-sensitive compound, such as various onium salts and quinonediazide compounds, to an aqueous alkali solution-soluble resin, such as a novolac resin, the resin having a phenolic hydroxyl group. The positive light-sensitive compound works in an image portion as an anti-dissolution agent which substantially decreases solubility of an aqueous alkali solution-soluble resin, and in a non-image portion develops no anti-dissolution ability but becomes development-removable due to heat. An image can thus be formed.

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[0004] Also, a positive light-sensitive image-forming material described in WO97/39894 and EP0823327A2 comprises a material which absorbs light to generate heat and a resin whose solubility in an aqueous alkali solution is changed by heat. The resin has poor solubility in an aqueous alkali solution in the image portion, but is increased in solubility in an aqueous alkali solution and becomes removable by developing due to heat in the non-image portion, and thus an image can be formed.

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[0005] In planographic printing plates currently in use, a novolac resin is particularly preferably used for the reason that it has a large difference in solubility in a developing solution between the exposed portion and the unexposed portion and high ink-receiving ability because it strongly interacts with an anti-dissolution agent. A novolac resin is preferably also used in positive light-sensitive image-forming materials for an infrared laser for the same reason.

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[0006] However, when a positive light-sensitive image-forming material using such a novolac resin is put in a molten condition and applied to a suitable support, dried and solidified to form a light-sensitive layer, thereby manufacturing a planographic printing plate, there is a problem concerning aging stability, that is, a reduction in sensitivity with the passing of time after the planographic printing plate has been manufactured. To deal with this problem, techniques for improving stability and printing durability by increasing the molecular weight of a novolac resin to be used have been proposed. However, because novolac resins currently in use are synthesized by reacting phenols with aldehydes using an acid as a catalyst, and the phenols are trifunctional, these resins pose the problem that a branched structure in the resin increases with an increase in the molecular weight of the resin to form a gel. In the case of using the resin for a planographic printing plate, the sensitivity is decreased when the molecular weight exceeds 10,000 and it is difficult to manufacture the planographic printing plate substantially stably.

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[0007] Also, in WO99/21715, a method in which a light-sensitive layer is applied to a support and dried, and then heat-treated for several days to forcibly change and stabilize the layer. However, this method poses the problem that it has poor adaptability for manufacturing, taking required time and energy into consideration. Therefore, image-forming materials which allow both sensitivity and aging stability and which have high adaptability for manufacturing have been desired.

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50 SUMMARY OF THE INVENTION

[0008] It is an object of the present invention to provide a positive planographic printing plate which has high sensitivity, has limited reduction in sensitivity with over and has high aging stability.

[0009] The inventors of the present invention have made studies to attain the above object, as a result, have found that material change of a novolac resin caused by entropy relaxation over time can be efficiently prevented by using an aromatic ring having many substituents as a monomer that forms the novolac resin, and have completed the present invention.

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[0010] Further, a positive planographic printing plate according to the present invention has a light-sensitive layer,

which is composed of a light-sensitive image-forming material containing a novolac resin having xylenol in a monomer and a material which absorbs light and generates heat, formed on a support.

[0011] Also, the present invention provides a light-sensitive image-forming material used for positive image recording which has a xylenol monomer-containing novolac resin and a material which absorbs light and generates heat.

5 [0012] Although the action of the light-sensitive image-forming material of the present invention is not clear, it is thought to be as follows. Xylenol, which is a monomer constituting a novolac resin, has more functional groups than a usual phenol monomer. The presence of such a structural unit in molecules ensures that the novolac resin can exist stably in the light-sensitive layer, similarly to the case of increasing the molecular weight of the novolac resin, but, unlike the case of increasing the molecular weight of the novolac resin itself, a reduction in solubility is not observed.

10 It is therefore considered that high sensitization and aging stability can be attained at the same time.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0013] The present invention will be hereinafter explained in detail.

Novolac resin containing a xylenol monomer

[0014] A planographic printing master plate according to the present invention includes a novolac resin (hereinafter referred to as a xylenol-containing novolac resin, as the case may be) that contains xylenol as a monomer for the formation of a light-sensitive layer.

20 [0015] The novolac resin according to the present invention may be synthesized through a usual reaction process in which phenol is reacted with formaldehyde in the presence of an acid catalyst under normal pressure. The novolac resin according to the present invention is characterized by the use of xylenol either in addition to or in place of phenol and cresol as a monomer to be used as a starting material.

25 [0016] Xylenol in the novolac resin used in the present invention may have any structure among six isomers. However, 3,5-xylenol, 2,3-xylenol, 2,5-xylenol and 3,4-xylenol, which have relatively high melting points, are preferable in view of improvement in stability.

[0017] The weight average molecular weight of the xylenol-containing novolac resin is preferably 500 to 10,000. In a case where the weight average molecular weight is less than 500, only an insufficient effect of improving printing durability is obtained, whereas in a case where the weight average molecular weight exceeds 10,000, the developing ability tends to be decreased. Therefore, both these cases are undesirable.

35 [0018] No particular limitation is imposed on the content amount of the xylenol monomer. Even if the amount is small, the effect of improving aging stability will be observed, and is improved with increased amounts of xylenol. If the proportion of the xylenol-containing novolac resin in an alkali-soluble resin that forms the light-sensitive layer of the planographic printing master plate of the present invention is designated Y% by weight and the content of the xylenol monomer in the novolac resin is designated X% by weight, $X \times Y$ is preferably 500 or more ($X \times Y \geq 500$). Specifically, if all of the alkali-soluble resin is the xylenol-containing novolac resin ($Y = 100\%$ by weight), xylenol is preferably contained in an amount of 5% by weight or more in the novolac resin in view of effectiveness.

40 [0019] It is found that the developing ability tends to be decreased with increased amounts of xylenol. However, in this case, a good image can be formed by regulating activity of a developing agent. Also, because the printing durability tends to be improved with decreased developing ability, the content of xylenol may be selected appropriately according to the characteristics of the planographic printing master plate to be used.

45 [0020] The above xylenol-containing novolac resin is used in an amount of 10 to 99% by weight, preferably 15 to 95% by weight and particularly preferably 20 to 90% by weight in the total solids of the positive light-sensitive image-forming material (hereinafter referred to as "image-forming material" on occasion) that forms the light-sensitive layer of the planographic printing master plate of the present invention. If the amount of the alkali-soluble polymer compound to be added is less than 30% by weight, the durability of the recording layer will be impaired, and an amount exceeding 99% by weight is undesirable in view of both sensitivity and durability. It is to be noted that in the case where a material obtained by mixing "an alkali-soluble resin other than the xylenol-containing novolac resin according to the present invention", described later, with the xylenol-containing novolac resin according to the present invention is used as a binder to prepare the image-forming material of the present invention, the binder as a whole is preferably contained in the total solid content of the image-forming material within the above-defined range. *Alkali-soluble resin other than the xylenol-containing novolac resin according to the present invention*

55 [0021] In the present invention, the aforementioned specific novolac resin is essential as the binder and may be used in combination with other alkali-soluble resins insofar as the effects of the present invention are not impaired.

[0022] Examples of other alkali-soluble resins (hereinafter referred to simply as "other alkali-soluble resins") which may be used by mixing with the above novolac resin include various alkali-soluble polymer compounds such as known and common novolac resins (containing no xylenol monomer), phenol-modified xylene resins, polyhydroxystyrene,

polyhydroxystyrene halide, acrylic resins having a phenolic hydroxyl group as disclosed in the publication of JP-A No. 51-34711, acrylic resins containing a sulfonamide group as described in the publication of JP-A No. 2-866 and urethane type resins.

[0023] Examples of common novolac resins having a weight average molecular weight of about 12,000 or less which may be used in the present invention include conventionally known novolac resins such as phenolformaldehyde resins and cresolformaldehyde resins, e.g., m-cresolformaldehyde resins, p-cresolformaldehyde resins, o-cresolformaldehyde resins, m-/p-mixed cresolformaldehyde resins and phenol/cresol (which may be any one of m-, p-, o- or mixed m-/p-, m-/o- or o-/p-) mixed formaldehyde resins.

[0024] As the urethane type resin, compounds described in the publications of JP-A Nos. 63-124047, 63-261350, 63-287942, 63-287943, 63-287944, 63-287946, 63-287947, 63-287948, 63-287949, 1-134354 and 1-255854 are preferably used.

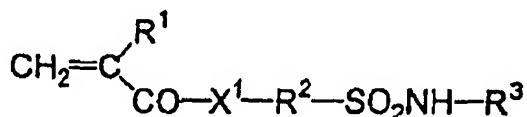
[0025] In the present invention, particularly preferable examples of the other alkali-soluble resin include polymer compounds having any one functional group of (a-1) phenolic hydroxyl groups, (a-2) sulfonamide groups and (a-3) active imide groups. For example, the following compounds may be exemplified.

[0026] As the polymer compound having the aforementioned (a-1) phenolic hydroxyl group, polymer compounds having a phenolic hydroxyl group at a side chain may be used. Examples of the polymer compound having the phenolic hydroxyl group at the side chain include polymer compounds obtained either by homopolymerizing a polymerizable monomer that includes a low molecular weight compound having one or more phenolic hydroxyl groups and one or more polymerizable unsaturated bonds or by copolymerizing the above monomer with another polymerizable monomer. Examples of the polymerizable monomer having a phenolic hydroxyl group include acrylamides, methacrylamides, acrylates, methacrylates and hydroxystyrene which contain a phenolic hydroxyl group. Specific examples of compounds which may be preferably used as the polymerizable monomer include N-(2-hydroxyphenyl)acrylamide, N-(3-hydroxyphenyl)acrylamide, N-(4-hydroxyphenyl)acrylamide, N-(2-hydroxyphenyl)methacrylamide, N-(3-hydroxyphenyl)methacrylamide, N-(4-hydroxyphenyl)methacrylamide, o-hydroxyphenylacrylate, m-hydroxyphenylacrylate, p-hydroxyphenylacrylate, o-hydroxyphenylmethacrylate, m-hydroxyphenylmethacrylate, p-hydroxyphenylmethacrylate, o-hydroxystyrene, m-hydroxystyrene, p-hydroxystyrene, 2-(2-hydroxyphenyl)ethylacrylate, 2-(3-hydroxyphenyl)ethylacrylate, 2-(4-hydroxyphenyl)ethylacrylate, 2-(2-hydroxyphenyl)ethylmethacrylate, 2-(3-hydroxyphenyl)ethylmethacrylate and 2-(4-hydroxyphenyl)ethylmethacrylate.

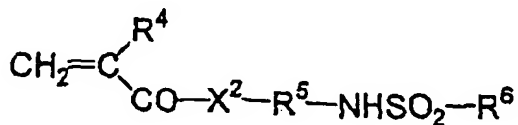
[0027] These resins having a phenolic hydroxyl group may be used either singly or in combinations of two or more.

[0028] A polymer compound having the above (a-2) sulfonamide group may be a polymer compound obtained either by homopolymerizing a polymerizable monomer having a sulfonamide group or by copolymerizing the above monomer with another polymerizable monomer. Given as examples of the polymerizable monomer having a sulfonamide group are polymerizable monomers including a low molecular weight compound having one or more sulfonamide groups -NH-SO₂- in which at least one hydrogen atom is bonded to a nitrogen atom, and one or more polymerizable unsaturated bonds. Among these polymerizable monomers, low molecular weight compounds having an acryloyl group, allyl group or vinyloxy group and a substituted or monosubstituted aminosulfonyl group or substituted sulfonylimino group are preferable.

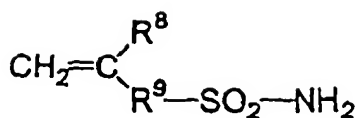
[0029] Given as examples of such compounds are compounds represented by the following formulae (a) to (e), which, however, are not intended to limit the present invention.



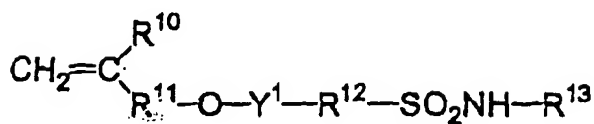
Formula (a)



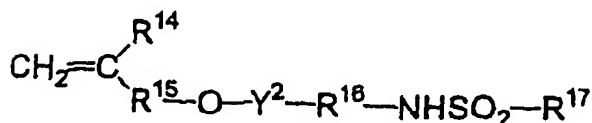
Formula (b)



Formula (c)



Formula (d)

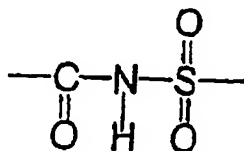


Formula (e)

wherein X¹ and X² respectively represent an oxygen atom or NR⁷; R¹ and R⁴ respectively represent a hydrogen atom or CH₃; R², R⁵, R⁹, R¹² and R¹⁶ respectively represent an alkylene group, a cycloalkylene group, an arylene group or an aralkylene group, which respectively have 1 to 12 carbon atoms and may have a substituent; R³, R⁷ and R¹³ respectively represent a hydrogen atom or an alkyl group, a cycloalkyl group, an aryl group or an aralkyl group, which respectively have 1 to 12 carbon atoms and may have a substituent; R⁶ and R¹⁷ respectively represent an alkyl group, a cycloalkyl group, an aryl group or an aralkyl group, which respectively have 1 to 12 carbon atoms and may have a substituent; R⁸, R¹⁰ and R¹⁴ respectively represent a hydrogen atom or CH₃; R¹¹ and R¹⁵ respectively represent an alkylene group, a cycloalkylene group, an arylene group or an aralkylene group, which respectively have 1 to 12 carbon atoms and may have a single bond or a substituent; and Y¹ and Y² respectively represent a single bond or CO.

[0030] Among these compounds, m-aminosulfonylphenylmethacrylate, N-(p-aminosulfonylphenyl)methacrylamide and N-(p-aminosulfonylphenyl)acrylamide may be preferably used.

[0031] Polymer compounds having the (a-3) active imide group are those having an active imide group represented by the following formula within a molecule. Examples of the polymer compound include polymer compounds obtained either by homopolymerizing a polymerizable monomer comprising a low molecular weight compound that has one or more active imino groups and one or more polymerizable unsaturated bonds, or by copolymerizing the polymerizable monomer with another polymerizable monomer.



[0032] As such a compound, specifically, N-(p-toluenesulfonyl)methacrylamide, N-(p-toluenesulfonyl)acrylamide or the like is preferably used.

[0033] As the other alkali-soluble resin, polymer compounds obtained by polymerizing two or more types among the aforementioned polymerizable monomers having a phenolic hydroxyl group, polymerizable monomers having a sulfonamide group and polymerizable monomers having an active imide group and polymer compounds obtained by copolymerizing two or more of these polymerizable monomers with another polymerizable monomer may be used.

[0034] In the case of copolymerizing a polymerizable monomer having a phenolic hydroxyl group with a polymerizable monomer having a sulfonamide group and/or a polymerizable monomer having an active imide group, the ratio of these components to be compounded is in a range preferably from 50:50 to 5:95 and particularly preferably from 40:60 to 10:90.

[0035] If the other alkali-soluble resin is a copolymer of the aforementioned polymerizable monomers having a phe-

nolic hydroxyl group, polymerizable monomers having a sulfonamide group and polymerizable monomers having an active imide group, the copolymer preferably contains a monomer which affords alkali-solubility in an amount of 10 mol% or more and the copolymer more preferably contains such a monomer in an amount of 20 mol% or more. If the amount of the copolymer component is less than 10 mol%, only insufficient alkali-solubility tends to be obtained, and there may be cases where the effect of improving the developing latitude is insufficiently produced.

[0036] As the monomer component to be copolymerized with the aforementioned polymerizable monomer having a phenolic hydroxyl group, polymerizable monomer having a sulfonamide group or polymerizable monomer having an active imide group, for example, monomers given in the following (1) to (12) may be used. However, the present invention is not limited to these monomers.

- (1) Acrylates and methacrylates having an aliphatic hydroxyl group such as 2-hydroxyethylacrylate or 2-hydroxyethylmethacrylate.
- (2) Alkylacrylates such as methylacrylate, ethylacrylate, propylacrylate, butylacrylate, amylacrylate, hexylacrylate, octylacrylate, benzylacrylate, 2-chloroethylacrylate, glycidylacrylate and N-dimethylaminoethylacrylate.
- (3) Alkylmethacrylates such as methylmethacrylate, ethylmethacrylate, propylmethacrylate, butylmethacrylate, amylmethacrylate, hexylmethacrylate, cyclohexylmethacrylate, benzylmethacrylate, 2-chloroethylmethacrylate, glycidylmethacrylate and N-dimethylaminoethylmethacrylate.
- (4) Acrylamides or methacrylamides such as acrylamide, methacrylamide, N-methylolacrylamide, N-ethylacrylamide, N-hexylmethacrylamide, N-cyclohexylacrylamide, N-hydroxyethylacrylamide, N-phenylacrylamide, N-nitrophenylacrylamide and N-ethyl-N-phenylacrylamide.
- (5) Vinyl ethers such as ethyl vinyl ether, 2-chloroethyl vinyl ether, hydroxyethyl vinyl ether, propyl vinyl ether, butyl vinyl ether, octyl vinyl ether and phenyl vinyl ether.
- (6) Vinyl esters such as vinyl acetate, vinyl chloroacetate, vinyl butyrate and vinyl benzoate.
- (7) Styrenes such as styrene, α -methylstyrene, methylstyrene and chloromethylstyrene.
- (8) Vinyl ketones such as methyl vinyl ketone, ethyl vinyl ketone, propyl vinyl ketone and phenyl vinyl ketone.
- (9) Olefins such as ethylene, propylene, isobutylene, butadiene and isoprene.
- (10) N-vinylpyrrolidone, N-vinylcarbazole, 4-vinylpyridine, acrylonitrile and methacrylonitrile.
- (11) Unsaturated imides such as maleimide, N-acryloylacrylamide, N-acetylmethacrylamide, N-propionylmethacrylamide and N-(p-chlorobenzoyl)methacrylamide.
- (12) Unsaturated carboxylic acids such as acrylic acid, methacrylic acid, maleic acid anhydride and itaconic acid.

[0037] If the other alkali-soluble resin is a homopolymer or copolymer of the aforementioned polymerizable monomer having a phenolic hydroxyl group, polymerizable monomer having a sulfonamide group or polymerizable monomer having an active imide group, a homopolymer or copolymer having a weight average molecular weight of 2,000 or more and a number average molecular weight of 500 or more is preferable. Homopolymers or copolymers having a weight average molecular weight of 5,000 to 300,000, a number average molecular weight of 800 to 250,000 and a degree of dispersion (weight average molecular weight/number average molecular weight) of 1.1 to 10 are more preferable.

[0038] These other alkali-soluble resins may be used singly or in combinations of two or more. The ratio of the alkali-soluble resin to the xylenol-containing novolac resin according to the present invention is preferably 0.05/1 to 1/0.1 and more preferably 0.1/1 to 1/0.2.

Materials which absorb light and generate heat

[0039] In the present invention, various pigments or dyes may be added as a material which absorbs light and generates heat.

[0040] As a pigment, commercially available pigments and pigments described in Color Index (C.I.) Handbook, "Latest Pigment Handbook" (edited by Japan Pigment Technological Association, published in 1977), "Latest Pigment Applied Technology" (CMC Shuppan, published in 1986) and "Printing Ink Technology" (CMC Shuppan, published in 1984) may be utilized.

[0041] Examples of the type of pigment include black pigments, yellow pigments, orange pigments, brown pigments, red pigments, violet pigments, blue pigments, green pigments, fluorescent pigments, metal powder pigments and other polymer-bound dyes. Specific examples of pigments which may be used in the present invention include insoluble azo pigments, azo lake pigments, condensed azo pigments, chelate azo pigments, phthalocyanine type pigments, anthraquinone type pigments, perillene and perinone type pigments, thioindigo type pigments, quinacridone type pigments, dioxazine type pigments, isoindolinone type pigments, quinophthalone type pigments, dyeing lake pigments, azine pigments, nitroso pigments, nitro pigments, natural pigments, fluorescent pigments, inorganic pigments, carbon black and the like.

[0042] Each of these pigments may be used either without carrying out a surface treatment thereon or after a surface treatment. As a surface-treating method, it is possible to use a method in which the surface is coated with a resin or wax, a method in which a surfactant is allowed to adhere to the surface or a method in which a reactive material (e.g., silane coupling agents, epoxy compounds and polyisocyanates) is bound to the surface of the pigment. The aforementioned surface treating methods are described in "Qualities and Applications of Metal Soaps" (Saiwai Shobou), "Printing Ink Technology" (CMC Shuppan, published in 1984) and "Latest Pigment Applied Technology" (CMC Shuppan, published in 1986).

[0043] The particle diameter of the pigment is in a range preferably from 0.01 μm to 10 μm , more preferably from 0.05 μm to 1 μm and particularly preferably 0.1 μm to 1 μm . It is undesirable if the particle diameter of the pigment is less than 0.01 μm in view of stability of dispersion in the light-sensitive layer coating solution, and it is undesirable if the particle diameter exceeds 10 μm in view of uniformity of the light-sensitive layer.

[0044] As a method of dispersing the pigment, known dispersing techniques that are used in the manufacturing of ink or the production of toner may be used. Examples of a dispersing machine include an ultrasonic dispersing machine, sand mill, attritor, pearl mill, super mill, ball mill, impeller, disperser, KD mill, colloid mill, dynatron, three-roll mill and pressure kneader. The details are described in "Latest Pigment Applied Technology" (CMC Shuppan, published in 1986).

[0045] As the dye, commercially available dyes and known dyes described in the literature (e.g., "Dye Handbook", edited by Organic Synthetic Chemical Association, published in 1970) may be utilized. Specific examples of the dye include azo dyes, metal complex salt azo dyes, pyrazolone azo dyes, anthraquinone dyes, phthalocyanine dyes, carbonium dyes, quinoneimine dyes, methine dyes and cyanine dyes.

[0046] In the present invention, among these pigments and dyes, those that absorb infrared light or near-infrared light are particularly preferable in view of adaptability for use with a laser which emits infrared light or near-infrared light.

[0047] Carbon black can be preferably used as such a pigment which absorbs infrared light or near-infrared light. Examples of dyes which absorb infrared light or near-infrared light include cyanine dyes described in JP-A Nos. 58-125246, 59-84356, 59-202829, 60-78787 and the like, methine dyes described in JP-A Nos. 58-173696, 58-181690, 58-194595 and the like, naphthoquinone dyes described in JP-A Nos. 58-112793, 58-224793, 59-48187, 59-73996, 60-52940, 60-63744 and the like, squarylium dyes described in JP-A No. 58-112792, cyanine dyes described in U.K. Patent No. 434,875 and dihydroperimidinesquarylium dyes described in U.S. Patent No. 5,380,635.

[0048] Also, near-infrared absorption sensitizing agents described in U.S. Patent No. 5,156,938 can be preferably used as the dye. Substituted arylbenzo(thio)pyrylium salts described in U.S. Patent No. 3,881,924, trimethinethiopyrylium salts described in JP-A No. 57-142645 (U.S. Patent No. 4,327,169), pyrylium type compounds described in JP-A Nos. 58-181051, 58-220143, 59-41363, 59-84248, 59-84249, 59-146063 and 59-146061, cyanine dyes described in JP-A No. 59-216146, pentamethinethiopyrylium salts described in U.S. Patent No. 4,283,475 and pyrylium compounds disclosed in the publications of JP-B Nos. 5-13514 and 5-19702 and, as commercially available products, Epolight III-178, Epolight III-130, Epolight III-125 and Epolight IV-62A (manufactured by Epolin) are used particularly preferably.

[0049] Also, particularly preferable examples of the dye may include near-infrared absorbing dyes represented by the formulae (I) and (II) in the specification of U.S. Patent No. 4,756,993.

[0050] Each of these pigments or dyes may be added in an amount of 0.01 to 50% by weight and preferably 0.1 to 10% by weight, and particularly preferably 0.5 to 10% by weight in the case of the dye and 1 to 10% by weight in the case of the pigment, with respect to total solids of the image-forming material which forms the light-sensitive layer. If the amount of the pigment or dye to be added is less than 0.01% by weight, the sensitivity will be low, whereas if the amount exceeds 50% by weight, the uniformity of the resulting light-sensitive layer will be lost and the durability of the light-sensitive layer will be impaired.

[0051] Each of these dyes or pigments may be added to the same layer as other components. Alternatively, a separate layer may be formed and each of these dyes or pigments added to the separate layer. In the case of adding to the separate layer, the dye or the pigment is desirably added to a layer adjacent to the layer containing the material which substantially decreases the solubility of the binding agent, which is heat-decomposable as explained later, provided that the binding agent is not decomposed.

Other components

[0052] Various additives may be further added to the image-forming material used to form the light-sensitive layer in the present invention as necessary. It is desirable to jointly use materials, such as onium salts, aromatic sulfone compounds and aromatic sulfonate compounds, which are heat-decomposable and substantially lower the solubility of the alkali-soluble polymer compound, provided that it is not decomposed, in view of improving resistance to dissolution in a developing solution of an image portion.

[0053] Examples of the onium salt may include diazonium salts, ammonium salts, phosphonium salts, iodonium

salts, sulfonium salts, selenonium salts and arsonium salts.

[0054] Preferable examples of the onium salt used in the present invention include diazonium salts described in S. I. Schlesinger, *Photogr. Sci. Eng.*, 18, 387 (1974), T.S. Bal et al., *Polymer*, 21, 423 (1980) and the publication of JP-A No. 5-158230; ammonium salts described in the specifications of U.S. Patent Nos. 4, 069, 055 and 4, 069, 056 and JP-A No. 3-140140; phosphonium salts described in D.C. Necker et al., *Macromolecules*, 17, 2468 (1984), C.S. Wen et al., *Teh, Proc. Conf. Rad. Curing ASIA*, p478 Tokyo, Oct (1988) and U.S. Patent Nos. 4,069,055 and 4,069,056; iodonium salts described in J.V. Crivello et al., *Macromolecules*, 10(6), 1307 (1977), *Chem. & Eng. News*, Nov. 28, p31 (1988), European Patent No. 104,143, U.S. Patent Nos. 4,339,049 and 4,410,201, JP-A Nos. 2-150848 and 2-296514, sulfonium salts described in J.V. Crivello et al., *Polymer J.* 17, 73 (1985), J.V. Crivello et al., *J. Org. Chem.*, 43, 3055 (1978), W.R. Watt et al., *J. Polymer Sci., Polymer Chem. Ed.*, 22, 1789 (1984), J.V. Crivello et al., *Polymer Bull.*, 14, 279 (1985), J.V. Crivello et al., *Macromolecules*, 14 (5), 1141 (1981), J.V. Crivello et al., *J. Polymer Sci., Polymer Chem. Ed.*, 17, 2877 (1979), European Patent Nos. 370,693, 233,567, 297,443 and 297,442, U.S. Patent Nos. 4,933,377, 3,902,114, 4,410,201, 4,339,049, 4,760,013, 4,734,444 and 2,833,827, German Patent Nos. 2,904,626, 3,604,580 and 3,604,581, selenium salts described in J.V. Crivello et al., *Macromolecules*, 10(6), 1307 (1977), J.V. Crivello et al., *J. Polymer Sci., Polymer Chem. Ed.*, 17, 1047 (1979) and arsonium salts described in C.S. Wen et al., *Teh, Proc. Conf. Rad. Curing ASIA*, p478 Tokyo, Oct (1988).

[0055] Examples of a counter ion of the onium salt may include tetrafluoroborate, hexafluorophosphate, triisopropyl naphthalenesulfonic acid, 5-nitro-o-toluenesulfonic acid, 5-sulfosalicylic acid, 2,5-dimethylbenzenesulfonic acid, 2,4,6-trimethylbenzenesulfonic acid, 2-nitrobenzenesulfonic acid, 3-chlorobenzenesulfonic acid, 3-bromobenzenesulfonic acid, 2-fluorocapryl naphthalenesulfonic acid, dodecylbenzenesulfonic acid, 1-naphthol-5-sulfonic acid, 2-methoxy-4-hydroxy-5-benzoyl-benzenesulfonic acid, paratoluenesulfonic acid and the like. Among these compounds, particularly hexafluorophosphoric acid and alkyl aromatic sulfonic acids such as triisopropyl naphthalenesulfonic acid and 2,5-dimethylbenzenesulfonic acid are desirable.

[0056] The amount of the additive onium salt compounded is preferably 1 to 50% by weight, more preferably 5 to 30% by weight and particularly preferably 10 to 30% by weight in the total solids of the image-forming material.

[0057] In the present invention, these additives and the binder are preferably contained in the same layer.

[0058] Also, cyclic acid anhydrides, phenols and organic acids may be used together for the purpose of improving sensitivity. As the cyclic acid anhydride, phthalic acid anhydride, tetrahydrophthalic acid anhydride, hexahydrophthalic acid anhydride, 3,6-endoxy- Δ^4 -tetrahydrophthalic acid anhydride, tetrachlorophthalic acid anhydride, maleic acid anhydride, chloromaleic acid anhydride, α -phenylmaleic acid anhydride, succinic acid anhydride and pyromellitic acid anhydride as described in the specification of U.S. Patent No. 4,115,128 may be used. Examples of the phenols include bisphenol A, p-nitrophenol, p-ethoxyphenol, 2,4,4'-trihydroxybenzophenone, 2,3,4-trihydroxybenzophenone, 4-hydroxybenzophenone, 4,4',4''-trihydroxytriphenylmethane and 4,4',3'',4''-tetrahydroxy-3,5,3',5'-tetramethyltriphenylmethane. Examples of the organic acids include sulfonic acids, sulfinic acids, alkyl sulfates, phosphonic acids, phosphates and carboxylic acids as described in, for example, the publications of JP-A Nos. 60-88942 and 2-96755. Given as specific examples of the organic acids are p-toluenesulfonic acid, dodecylbenzenesulfonic acid, p-toluenesulfinic acid, ethylsulfuric acid, phenylphosphonic acid, phenylphosphinic acid, phenyl phosphate, diphenyl phosphate, benzoic acid, isophthalic acid, adipic acid, p-toluic acid, 3,4-dimethoxybenzoic acid, phthalic acid, terephthalic acid, 4-cyclohexene-1,2-dicarboxylic acid, erucic acid, lauric acid, n-undecanoic acid and ascorbic acid.

[0059] The proportion of the aforementioned cyclic acid anhydride, phenols and organic acids in the total solid of the image-forming material is preferably 0.05 to 20% by weight, more preferably 0.1 to 15% by weight and particularly preferably 0.1 to 10% by weight.

[0060] A nonionic surfactant as described in the publications of JP-A Nos. 62-251740 and 3-208514 and an amphoteric surfactant as described in the publications of JP-A Nos. 59-121044 and 4-13149 may be added to the image-forming material according to the present invention to widen the range of stability to developing conditions.

[0061] Specific examples of the nonionic surfactant include sorbitan tristearate, sorbitan monopalmitate, sorbitan trioleate, monoglyceride stearate and polyoxyethylenenonyl phenyl ether.

[0062] Specific examples of the amphoteric surfactant include alkyl di(aminoethyl)glycine, alkyl polyaminoethylglycine hydrochloride, 2-alkyl-N-carboxyethyl-N-hydroxyethylimidazolium betaine and N-tetradecyl-N,N-betaine (e.g., trademark: "Amorgen K", manufactured by Dai-ichi Kogyo).

[0063] The proportion of the above nonionic surfactant and amphoteric surfactant in the image-forming material is preferably 0.05 to 15% by weight and more preferably 0.1 to 5% by weight.

[0064] A printing-out agent, used to obtain a visible image directly after heat-treatment by exposure, and dyes or pigments used as image colorants may be added to the image-forming material of the present invention.

[0065] Given as typical examples of the printing-out agent are combinations of a compound which releases an acid when heated in exposure (optically acid-releasable agent) and an organic dye capable of producing a salt. Specific examples of these combinations include combinations of o-naphthoquinonediazide-4-sulfonic acid halogenide and a salt-formable organic dye as described in the publications of JP-A Nos. 50-36209 and 53-8128 and combinations of a

trihalomethyl compound and a salt-formable organic dye as described in the publications of JP-A Nos. 53-36223, 54-74728, 60-3626, 61-143748, 61-151644 and 63-58440. Such trihalomethyl compounds include oxazole type compounds and triazine type compounds, which have high aging stability and provide a clear print-out image.

[0066] As the image-colorant, other dyes may be used in addition to the aforementioned salt-formable organic dyes.

- 5 Preferable dyes may include oil-soluble dyes and basic dyes, including the salt-formable organic dyes. Specific examples may include Oil Yellow #101, Oil Yellow #103, Oil Pink #312, Oil Green BG, Oil Blue BOS, Oil Blue #603, Oil Black BY, Oil Black BS and Oil Black T-505 (manufactured by Orient Kagaku Kogyo), Victoria Pure Blue, Crystal Violet (CI42555), Methyl Violet (CI42535), Ethyl Violet, Rhodamine B (CI145170B), Malachite Green (CI42000) and Methylene Blue (CI52015). Also, dyes described in the publication of JP-A No. 62-293247 are particularly preferable. These
- 10 dyes may be added in a proportion of 0.01 to 10% by weight and more preferably 0.1 to 3% by weight in the total solids of the image-forming material.

[0067] A plasticizer may be added as required to the image-forming material of the present invention, to impart softness and the like of a coating film. For example, butylphthalyl, polyethylene glycol, tributyl citrate, diethyl phthalate, dibutyl phthalate, dihexyl phthalate, dioctyl phthalate, tricresyl phosphate, tributyl phosphate, trioctyl phosphate, tetrahydrofurfuryl oleate, oligomers or polymers of acrylic acid or methacrylic acid, and the like may be used.

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[0068] The image-forming material of the present invention is generally formed by dissolving each above component in a solvent to form a coating solution and applying the solution to an appropriate support. The positive planographic printing plate of the present invention can be produced by forming the light-sensitive layer in this manner. Examples of the solvent to be used here may include, but are not limited to, ethylene dichloride, cyclohexanone, methyl ethyl ketone, methanol, ethanol, propanol, ethylene glycol monomethyl ether, 1-methoxy-2-propanol, 2-methoxyethyl acetate, 1-methoxy-2-propyl acetate, dimethoxyethane, methyl lactate, ethyl lactate, N,N-dimethylacetamide, N,N-dimethylformamide, tetramethylurea, N-methylpyrrolidone, dimethylsulfoxide, sulfolane, γ -butyrolactone and toluene. These solvents may be used either singly or as mixtures. The concentration of the above component (total solid including additives) in the coating solution is preferably 1 to 50% by weight. The amount (solid content) of the coating solution

20 applied to the support, after the coating solution is applied and dried, is generally preferably 0.5 to 5.0 g/m² in the case of a positive planographic printing master plate, though this may vary depending on use. As a coating method, various methods may be used. Examples of these methods may include bar coater coating, rotating coating, spray coating, curtain coating, dip coating, air-knife coating, blade coating and roll coating. With a decreased coating amount, apparent sensitivity will be increased but the film characteristics of the light-sensitive layer will be low.

[0069] A surfactant such as a fluorine type surfactant as described in JP-A No. 62-170950 may be added to the coating solution for the image-forming material of the present invention to improve coatability. The amount to be added is preferably 0.01 to 1% by weight and more preferably 0.05 to 0.5% by weight in the total solid of the light-sensitive layer.

[0070] Examples of the support to be used in the present invention include dimensionally stable plate materials such as paper, paper on which a plastic (e.g., polyethylene, polypropylene or polystyrene) is laminated, metal plates (e.g., aluminum, zinc and copper), plastic films (e.g., cellulose diacetate, cellulose triacetate, cellulose propionate, cellulose butylate, cellulose acetate butylate, cellulose nitrate, polyethylene terephthalate, polyethylene, polystyrene, polypropylene, polycarbonate and polyvinylacetal) and paper on which a metal as aforementioned is laminated or deposited, plastic films and the like.

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[0071] As the support in the present invention, polyester films or aluminum plates are desirable. Among these materials, aluminum plates, which are dimensionally stable and relatively inexpensive, are particularly preferable. Preferable aluminum plates are pure aluminum plates and alloy plates having aluminum as their major component and containing minute amounts of foreign elements, and may be plastic films on which aluminum is laminated or deposited. The foreign elements contained in an aluminum alloy may include silicon, iron, manganese, copper, magnesium, chromium, zinc, bismuth, nickel and titanium. The content of the foreign elements is a maximum of 10% by weight. Aluminum

40 which is particularly preferable as the support in the present invention is pure aluminum. However, it is difficult to obtain perfectly pure aluminum because of difficulties in refining techniques, and therefore aluminum containing minute amounts of foreign elements is acceptable. The composition of an aluminum plate to be applied as the support in the present invention in this manner is not specified, and conventionally known and commonly used aluminum plate materials may be used. The thickness of the aluminum plate used for the support in the present invention is about 0.1

45 mm to 0.6 mm, preferably 0.15 mm to 0.4 mm and particularly preferably 0.2 mm to 0.3 mm.

[0072] A degreasing treatment of the aluminum plate by using, for example, a surfactant, an organic solvent or an aqueous alkaline solution is performed to remove rolling oil from the surface prior to roughing of the aluminum plate, as necessary.

[0073] The treatment of roughing the surface of the aluminum plate may be carried out using various methods, such as a method of roughing mechanically, a method of roughing by dissolving the surface electrochemically and a method of selectively dissolving the surface chemically. As the mechanical method, known methods such as a ball polishing method, brush polishing method, blast polishing method and buff polishing method may be used. On the other hand, as the electrochemical roughing method, there is a method in which the treatment is performed in a hydrochloric acid

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or nitric acid electrolyte using a.c. or d.c. current. Also, a combination of the above two kinds of method may be used, as disclosed in JP-A No. 54-63902.

[0074] The aluminum plate roughened in this manner is subjected to an alkali etching treatment and a neutralization treatment and thereafter to an anodic oxidation treatment to improve water-retentivity and wear resistance of the surface, as desired. As the electrolyte used for the anodic oxidation treatment of the aluminum plate, various electrolytes for forming a porous oxide film may be used and sulfuric acid, phosphoric acid, oxalic acid, chromic acid or mixed acids of these acids may usually be used. The density of each of these electrolytes is suitably determined according to the type of electrolyte.

[0075] The conditions of the anodic oxidation treatment vary depending upon the type of electrolyte and are not therefore specified in a general manner. However, each condition is preferably in the following ranges: concentration of the electrolyte, 1 to 80% by weight solution; liquid temperature, 5 to 70°C; current density, 5 to 60 A/dm²; voltage, 1 to 100 V; and electrolysis time, 10 seconds to 5 minutes.

[0076] If the amount of the anodic oxide film is smaller than 1.0 g/m², only insufficient printing durability is obtained and the non-image portion is easily flawed, which easily causes the so-called "flaw stains", specifically, ink is stuck to a flawed part during printing.

[0077] After the anodic oxidation treatment is performed, the surface of aluminum is subjected to hydrophilic treatment, as necessary. The hydrophilic treatment used in the present invention includes an alkali metal silicate (for example, an aqueous sodium silicate solution) method as disclosed in U.S. Patent Nos. 2,714,066, 3,181,461, 3,280,734 and 3,902,734. In this method, the support is treated by dipping in an aqueous sodium silicate solution, or treated electrolytically. Besides the above methods, for instance, a method of treating using potassium fluorozirconate as disclosed in JP-B No. 36-22063 or a method of treating using polyvinylphosphonic acid as disclosed in U.S. Patent Nos. 3,276,868, 4,153,461 and 4,689,272 can be used.

[0078] The positive planographic printing master plate of the present invention is a type in which a positive light-sensitive image-forming material is formed on a support. An undercoat layer may be formed between the support and the image-forming material as necessary.

[0079] As a component of the undercoat layer, various organic compounds can be used. The component may be selected from carboxymethyl cellulose, dextrin, gum arabic, phosphonic acids having an amino group such as 2-aminoethylphosphonic acid, organic phosphonic acids, which may have substituents, such as phenylphosphonic acid, naphthylphosphonic acid, alkylphosphonic acid, glycerophosphonic acid, methylenediphosphonic acid and ethylenediphosphonic acid, organic phosphoric acids, which may have substituents such as phenylphosphoric acid, naphthylphosphoric acid, alkylphosphoric acid and glycerophosphoric acid, organic phosphinic acids, which may have substituents, such as phenylphosphinic acid, naphthylphosphinic acid, alkylphosphinic acid and glycerophosphinic acid, amino acids such as glycine and β -alanine and hydrochlorides of amines having a hydroxyl group such as hydrochloride of triethanolamine. These organic compounds may be used as mixtures thereof.

[0080] This organic undercoat layer may be provided by the following method. Specifically, it is possible to adopt a method in which a solution, prepared by dissolving the above organic compound in water, an organic solvent such as methanol, ethanol or methyl ethyl ketone or a mixed solvent of these solvents, is applied to an aluminum plate and dried or a method in which an aluminum plate is dipped in a solution, prepared by dissolving the above organic compound in water, an organic solvent such as methanol, ethanol and methyl ethyl ketone or a mixed solvent of these solvents, to allow the above compound to adhere to the support, and thereafter the support is washed with water or the like and dried to form the organic undercoat layer. In the former method, a solution in which the concentration of the above organic compound is 0.005 to 10% by weight may be applied using various methods. In the latter method, the concentration of the solution is 0.01 to 20% by weight and preferably 0.05 to 5% by weight, the dipping temperature is 20 to 90°C and preferably 25 to 50°C and the dipping time is 0.1 seconds to 20 minutes and preferably 2 seconds to 1 minute. The solution used for this purpose can be adjusted to a pH ranging from 1 to 12 by using a basic material such as ammonia, triethylamine or potassium hydroxide or an acidic material such as hydrochloric acid or phosphoric acid. Also, a yellow dye may be added to improve the tone reproducibility of the image-forming material.

[0081] The amount of the organic undercoat layer to be applied is appropriately 2 to 200 mg/m² and preferably 5 to 100 mg/m². If the above coating amount is smaller than 2 mg/m², sufficient printing durability cannot be obtained, and if the amount is greater than 200 mg/m², the same result will occur.

[0082] The positive planographic printing plate manufactured in the above manner is usually subjected to image exposure and developing treatment.

[0083] As a light source of active rays to be used for the image exposure, light sources having an emission wavelength in the near-infrared to infrared region are preferable and a solid laser or a semiconductor laser is particularly preferable.

[0084] As the developing solution or replenishing solution used for the positive printing master plate of the present invention, conventionally known aqueous alkali solutions may be used. Given as examples of the aqueous alkali solution are solutions of inorganic alkali salts such as sodium silicate, potassium silicate, sodium tertiary phosphate, potassium tertiary phosphate, ammonium tertiary phosphate, sodium secondary phosphate, potassium secondary

phosphate, ammonium secondary phosphate, sodium carbonate, potassium carbonate, ammonium carbonate, sodium bicarbonate, potassium bicarbonate, ammonium bicarbonate, sodium borate, potassium borate, ammonium borate, sodium hydroxide, ammonium hydroxide, potassium hydroxide and lithium hydroxide. Also, organic alkali agents such as monomethylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, triethylamine, monoisopropylamine, diisopropylamine, triisopropylamine, n-butylamine, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, ethyleneimine, ethylenediamine and pyridine.

[0085] These alkaline agents may be used either singly or in combinations of two or more.

[0086] A particularly preferable developing agent among these alkaline agents is an aqueous solution of a silicate such as sodium silicate or potassium silicate. This is because developing ability can be controlled by the ratio and concentrations of silicon oxide (SiO_2) which is the silicate component and an alkali metal oxide (M_2O). For example, alkali metal silicates as described in the publications of JP-A No. 54-62004 and JP-B No. 57-7427 are effectively used.

[0087] It is known that when a developing operation is carried out using an automatic developing machine, a large number of planographic printing plates can be treated without exchanging a developing solution contained in a developing solution tank over a long period of time, by addition of an aqueous solution (replenishing solution) having higher alkalinity than the developing solution. In the present invention, this replenishing system is also preferably applied. Various surfactants and organic solvents may be added as required to the developing solution and the replenishing solution for purposes of promoting or suppressing developing ability, improving the dispersion of wastes produced by developing, and improving the affinity of the image portion of the printing plate to ink. Preferable examples of the surfactant include an anionic type, cationic type, nonionic type and amphoteric type.

[0088] A reducing agent, such as a sodium salt of an inorganic acid such as hydroquinone, resorcinol, sulfurous acid, hydrogen sulfuric acid, and further an organic carboxylic acid, an anti-foaming agent and a water softener may be added to the developing solution and replenishing solution as necessary.

[0089] The planographic printing plate which is developed using the above developing solution and replenishing solution is after-treated using a rinse solution containing washing water, a surfactant and the like, and an insensitization-greasing solution containing gum arabic and a starch derivative. As after-treatment in the case of using the image-forming material of the present invention for a printing plate, these treatments may be used in combination.

[0090] In plate-making and printing fields in recent years, an automatic developing machine for printing plates has been widely used for rationalization and standardization of plate-making works. This automatic developing machine usually consists of a developing section and an after-treatment section, including a system for conveying a planographic printing plate, respective process solution vessels and a spray system. In the developing machine, each process solution drawn by a pump is sprayed from a spray nozzle while an exposed printing plate is carried horizontally to carry out developing. Also, a method is known today in which a planographic printing plate is dipped and conveyed in a process solution vessel filled with a process solution by using, for example, a submerged guide roll. In such an automatic process, the printing plate may be treated while a replenishing solution is supplied to each process solution in response to throughput and operating time.

[0091] Also, a so-called nonreturnable treating system using a substantially unused process solution to carry out treatment can be applied.

[0092] If unnecessary image portions (e.g., a film edge mark of an original image film) are present on the planographic printing plate after image exposure, developing, washing with water and/or rinsing and/or gum-drawing are carried out, measures may be taken to erase the unnecessary image portions. As the above erasing method, a method in which an erasing liquid is applied to the unnecessary image portion and is allowed to stand as is for a fixed time, followed by washing with water as described in the publication of JP-B No. 2-13293 is preferable. However, a method in which active light rays guided by an optical fiber are applied to the unnecessary image portion, followed by developing as described in the publication of JP-A No. 59-174842 may also be utilized.

[0093] The planographic printing plate obtained in the above manner may be subjected to a printing step after an insensitization-greasing gum is applied as desired to the printing plate. A burning treatment may be performed for the purpose of making the planographic printing plate have more improved printing durability.

[0094] If the planographic printing plate is treated by burning, it is preferable to treat the planographic printing plate by using a surface regulating solution prior to the burning, as described in the publication of each of JP-B Nos. 61-2518, and 55-28062, and JP-A Nos. 62-31859 and 61-159655.

[0095] As the treating method, a method in which the surface regulating solution is applied to the surface of the printing plate using a sponge or absorbent cotton impregnated with the surface regulating solution, a method in which the planographic printing plate is immersed in a butt filled with the surface regulating solution to apply the solution to the planographic printing plate and a method of applying using an automatic coater may be used. Also, it is more preferable to make the applied amount uniform with a squeegee or a squeegee roller after the application is finished.

[0096] The amount of the surface regulating solution to be applied is appropriately 0.03 to 0.8 g/m² (dry weight).

[0097] The planographic printing plate coated with the surface regulating solution is dried and then heated to high temperatures by using a burning processor (e.g., Burning Processor: Product name "BP-1300") marketed by Fuji Photo

Film Co., Ltd. Heating temperature and time in this case are preferably in a range from 180 to 300°C and in a range from 1 to 20 minutes respectively, though these conditions will differ depending upon the types of component for forming an image.

[0098] The planographic printing plate which has been treated by burning may be subjected appropriately to treatments which are conventionally performed such as washing and gum-drawing as necessary. In cases where a surface regulating solution containing an aqueous polymer compound and the like is used, the so-called insensitization-greasing treatment, such as gum-drawing, can be omitted.

[0099] The planographic printing plate obtained by the aforementioned treatments is incorporated into an offset printer and used to print a number of sheets.

EXAMPLES

[0100] The present invention will be hereinafter explained in detail by way of examples, which, however, are not intended to be limiting of the present invention.

Examples 1 to 5, Comparative Example 1

Production of a planographic printing plate

[0101] A 0.3-mm-thick aluminum plate was washed with trichloroethylene to degrease. Then the surface of the aluminum plate was pebbled using a nylon brush and a 400 mesh pumice/water suspension and was then thoroughly washed with water. This plate was immersed in an aqueous 25% sodium hydroxide solution at 45°C for 9 seconds to carry out etching, followed by washing with water. The plate was further immersed in a 20% nitric acid solution for 20 seconds and then washed. At this time, the amount of etching of the pebbled surface was about 3 g/m². Next, the plate was formed with a 3 g/m² d.c. anodic oxidation film, using 7% sulfuric acid as an electrolyte at a current density of 15 A/dm². After that, the plate was washed with water and dried.

[0102] The resulting plate was treated in an aqueous solution of 2.5% by weight of sodium silicate at 30°C for 10 seconds and coated with the undercoat solution described below. The film was dried at 80°C for 15 seconds to obtain a support. The amount of the film applied was 15 mg/m² after drying.

[0103] The coating solution for a light-sensitive layer-forming solution was applied to the resulting support such that the amount applied was 1.5 g/m², to obtain planographic printing master plates 1 to 6. Planographic printing master plates produced using light-sensitive solutions 1 to 5 containing a xylene-containing novolac resin were designated as Examples 1 to 5 respectively. Also, a planographic printing master plate produced using a light-sensitive solution 6 containing a known novolac resin was obtained and designated as Comparative Example 1.

[0104] The mol ratio between monomers of a novolac resin to be used, the weight average molecular weight of the novolac resin and the amount of unreacted monomers are as follows.

- Novolac resin 1

Phenol/m-cresol/2,3-xylene (50/30/20)

Mw: 7,600, unreacted monomer: 0.8% by weight.

- Novolac resin 2

m-Cresol/p-cresol/3,5-xylene (30/30/40)

Mw: 2,500, unreacted monomer: 0.5% by weight.

- Novolac resin 3

m-Cresol/2,5-xylene (20/80)

Mw: 5,400, unreacted monomer: 0.6% by weight

- Novolac resin 4

Phenol/3,5-xylene (50/50)

Mw: 9,800, unreacted monomer: 1.0% by weight

- Novolac resin 5

m-Cresol/2,3-xyleneol (90/10)

Mw: 3,300, unreacted monomer: 0.5% by weight

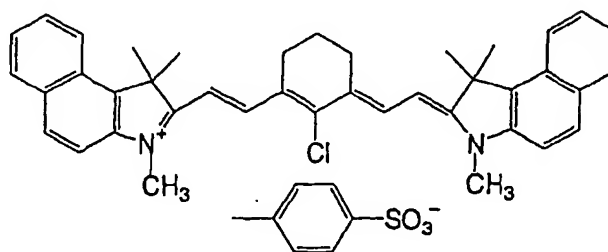
- Novolac resin 6

m-cresol/p-cresol (60/40)

Mw: 4,000, unreacted monomer: 0.5% by weight

[0105] Light-sensitive solutions 1 to 5

- Novolac resin (resin described in Table 1) 1.0 g
- Cyanine dye A (the structure shown below) 0.1 g
- Phthalic acid anhydride 0.05 g
- p-Toluenesulfonic acid 0.002 g
- Ethyl violet in which the counter ion was 6-hydroxy- β -naphthalenesulfonic acid 0.02 g
- Fluorine type surfactant (Product name: Megafac F-177, manufactured by Dainippon Ink and Chemicals) 0.05 g
- Methyl ethyl ketone 8 g
- 1-Methoxy-2-propanol 4 g



Cyanine dye A

Table 1

	Planographic printing plate	Light-sensitive solution	Novolac resin
Example 1	Planographic printing plate 1	Light-sensitive solution 1	Novolac resin 1
Example 2	Planographic printing plate 2	Light-sensitive solution 2	Novolac resin 2
Example 3	Planographic printing plate 3	Light-sensitive solution 3	Novolac resin 3
Example 4	Planographic printing plate 4	Light-sensitive solution 4	Novolac resin 4
Example 5	Planographic printing plate 5	Light-sensitive solution 5	Novolac resin 5
Comparative Example 1	Planographic printing plate 6	Light-sensitive solution 6	Novolac resin 6

Evaluation of planographic printing master plates

[0106] A part of each planographic printing master plate was packaged with craft paper and allowed to stand for 3 days in a thermostatic chamber at ambient temperature and at 45°C and a humidity of 75%. The aging for 3 days, during which each planographic printing master plate was stored in the thermostatic chamber, ensured that evaluation the same as for aging a planographic printing master plate stored at ambient temperature for a period from about several months to one year could be made. It is to be noted that a reduction in sensitivity when a planographic printing master plate is stored for 3 days at ambient temperature is almost unobservable, in general.

[0107] These planographic printing plates were exposed using a Plate Setter Trendsetter 3244F, manufactured by Kureo and developed using an automatic developing machine. As to conditions of exposure, a number of rotations

was fixed to 150 rpm and output power was changed in about 9% increments from 3 to 12 W to find clear sensitivity. The clear sensitivity is defined as a minimum energy required to dissolve an exposed portion perfectly, and the quantity of energy (E) is given by the following formula.

5

$$E = W \times 2350/\text{rpm} \quad (W: \text{output power, rpm: number of rotations})$$

[0108] 20 litres of an alkali developing process solution suitable for the respective planographic printing plate, among an alkali developing process solution A (pH: about 13) and an alkali developing process solution B (pH: about 13.2) respectively having the following compositions, was filled into a developing process vessel of a commercially available automatic developing machine LP-900H (manufactured by Fuji Photo Film Co., Ltd.) provided with a dipping-type developing vessel and kept at 30°C. 8 litres of tap water was laid in a second bath of the LP-900H and a finishing gum solution prepared by diluting FP-2W (manufactured by Fuji Photo Film Co., Ltd.) with water (1:1) was laid in a third bath of the LP-900H. The developing treatment of each of the planographic printing master plates 1 to 6 was carried out in the automatic developing machine provided with a developing process solution suitable for the planographic printing plate. The alkali developing process solution used here and the results of evaluation are shown in Table 2 below.

Composition of the alkali developing process solution A

20 [0109]

- $\text{SiO}_2 \cdot \text{K}_2\text{O}$ ($\text{K}_2\text{O}/\text{SiO}_2 = 1.1$ (mol ratio)) 4.0% by weight
- Citric acid 0.5% by weight
- Polyethylene glycol 0.5% by weight
- 25 (weight average molecular weight: 1,000)
- Water 95.0% by weight

Composition of the alkali developing process solution B:

30 [0110]

- $\text{SiO}_2 \cdot \text{K}_2\text{O}$ ($\text{K}_2\text{O}/\text{SiO}_2 = 1.1$ (mol ratio)) 8.0% by weight
- Citric acid 1.0% by weight
- Polyethylene glycol 1.0% by weight
- 35 (weight average molecular weight: 1,000)
- Water 90.0% by weight

Table 2

	Clear sensitivity (mJ/cm ²)			
	Alkali developing process solution A		Alkali developing process solution B	
	Ambient temperature aging	45°C, 75% humidity aging	Ambient temperature aging	45°C, 75% humidity aging
40				
45	Example 1	61	67	-
	Example 2	56	61	-
	Example 3	-	-	56
	Example 4	56	61	-
50	Example 5	51	56	-
	Comparative Example 1	79	122	-

55

[0111] As is clear from Table 2, the planographic printing master plates using xylene-containing novolac resins according to the present invention had high sensitivity and excellent stability with time. On the other hand, the Comparative Example provided with a light-sensitive layer having the same structure as the Examples except that a conventionally

known novolac resin was used had insufficient storage stability.

Examples 6 to 8 and Comparative Example 2

5 Synthesis of copolymer 1

[0112] A 500 ml three-neck flask equipped with a stirrer, a condenser tube and a dropping funnel was charged with 31.0 g (0.36 mol) of methacrylic acid, 39.1 g (0.36 mol) of ethyl chloroformate and 200 ml of acetonitrile and the mixture was stirred while it was cooled in an ice-water bath. 36.4 g (0.36 mol) of triethylamine was added dropwise to the mixture by using the dropping funnel over about one hour. After the dripping was finished, the ice-water bath was removed and the mixture was stirred at ambient temperature for 30 minutes.

[0113] 51.7 g (0.30 mol) of p-aminobenzenesulfonamide was added to the reaction mixture and the mixture was stirred for one hour while being heated at 70°C in an oil bath. After a reaction was finished, this mixture was poured into 1 litre of water while the water was stirred, and the resulting mixture was stirred for 30 minutes. This mixture was subjected to filtration to remove precipitate, which was then made into a slurry using 500 ml of water. Thereafter, the slurry was subjected to filtration and an obtained solid was dried to obtain a white solid of N-(p-aminosulfonylphenyl) methacrylamide (yield: 46.9 g).

[0114] Next, a 20 ml three-neck flask equipped with a stirrer, a condenser tube, and a dropping funnel was charged with 4.61 g (0.0192 mol) of the N-(p-aminosulfonylphenyl) methacrylamide, 2.58 g (0.0258 mol) of ethylmethacrylate, 0.80 g (0.015 mol) of acrylonitrile and 20 g of N,N-dimethylacetamide and this mixture was stirred at 65°C under heating in a hot water bath. 0.15 g of "V-65" (manufactured by Wako Pure Chemical Industries) was added to the mixture and the resulting mixture was stirred in a nitrogen stream for 2 hours while being kept at 65°C. A mixture of 4.61 g of N-(p-aminosulfonylphenyl) methacrylamide, 2.58 g of methylmethacrylate, 0.80 g of acrylonitrile, 20 g of N,N-dimethylacetamide and 0.15 g of "V-65" was further added dropwise to the reaction mixture over 2 hours using the dropping funnel. After the dripping was finished, the resulting mixture was further stirred at 65°C for 2 hours. After completion of a reaction, 40 g of methanol was added to the mixture, which was then cooled, and the resulting mixture was poured into 2 litres of water while the water was stirred. After this mixture was stirred for 30 minutes, a precipitate was taken out by filtration and dried to obtain 15 g of a white solid of a copolymer 1. The weight average molecular weight (polystyrene base) of this specified copolymer 1 was measured by gel permeation chromatography and the average molecular weight was found to be 54,000.

Production of a support

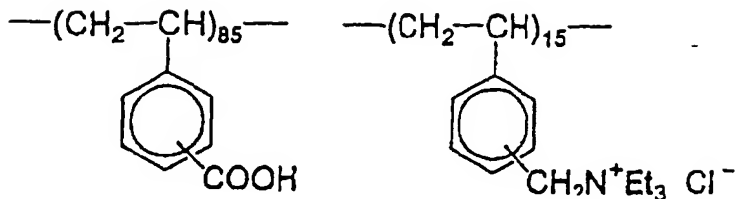
[0115] A 0.3-mm thick aluminum plate was washed with trichloroethylene to degrease. Then the surface of the aluminum plate was pebbled using a nylon brush and a 400 mesh pumice/water suspension and was then thoroughly washed with water. This plate was immersed in an aqueous 25% sodium hydroxide solution at 45°C for 9 seconds to carry out etching, followed by washing with water. The plate was further immersed in a 20% nitric acid solution for 20 seconds and then washed with water. At this time, the amount of etching of the pebbled surface was about 3 g/m². Next, the plate was formed with a 3 g/m² d.c. anodic oxidation film, using 7% sulfuric acid as an electrolyte at a current density of 15 A/dm². After that, the plate was washed with water and dried. The resulting plate was treated in an aqueous solution of 2.5% by weight of sodium silicate at 30°C for 10 seconds and coated with the following undercoat solution. The film was dried at 80°C for 15 seconds to obtain a support. The amount of the film applied was 15 mg/m² after drying.

45 Undercoat solution 2

[0116]

- Random copolymer P (shown below) having a molecular weight of 28,000 0.3 g
- 50 • Methanol 100 g
- Water 1 g

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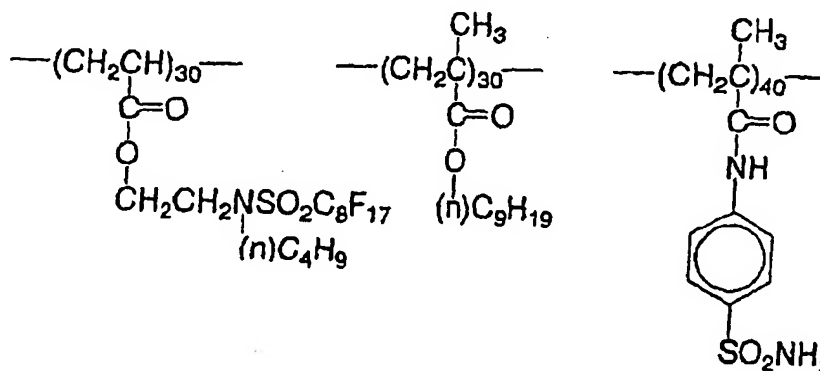
Structural units of random copolymer P

[0117] The following light-sensitive solution was prepared. The resulting support was coated with this light-sensitive solution such that the amount of the light-sensitive solution to be applied was 1.2 g/m², to obtain planographic printing master plates 7 to 10. Among these planographic printing master plates 7 to 10, those using light-sensitive solutions 7 to 9 using a xylenol-containing novolac resin were designated as Examples 6 to 8 respectively. Also, a planographic printing master plate produced using a light-sensitive solution 10 containing a known novolac resin was obtained and designated as Comparative Example 2.

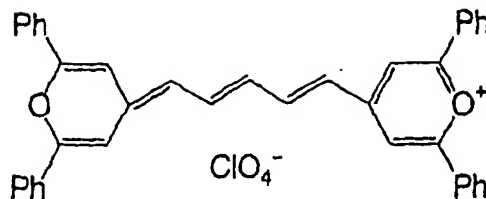
Light-sensitive solutions 7 to 10

[0118]

- Fluorine-containing polymer (the structure shown below) 0.03 g
- Copolymer 1 0.75 g
- Novolac resin (resin described in Table 3) 0.25 g
- p-Toluenesulfonic acid 0.003 g
- Tetrahydrophthalic acid anhydride 0.03 g
- Pyrylium dye B (the structure shown below) 0.017 g
- Dye in which the counter ion of Victoria Pure Blue BOH was 1-naphthalenesulfonic acid anion 0.015 g
- 3-methoxy-4-diazodiphenylaminehexafluorophosphate 0.02 g
- n-Dodecyl stearate 0.03 g
- Fluorine type surfactant 0.05 g
- (Product name: Megafac F-177, manufactured by Dainippon Ink and Chemicals)
- γ -butyrolactone 10 g
- Methyl ethyl ketone 10 g
- 1-Methoxy-2-propanol 8 g



Fluorine-containing polymer



Pyrylium dye B

Table 3

	Planographic printing plate	Light-sensitive solution	Novolac resin Novolacresin
Example 6	Planographic printing plate 7	Light-sensitive solution 7	Novolac resin 2
Example 7	Planographic printing plate 8	Light-sensitive solution 8	Novolac resin 3
Example 8	Planographic printing plate 9	Light-sensitive solution 9	Novolac resin 4
Comparative Example 2	Planographic printing plate 10	Light-sensitive solution 10	Novolac resin 6

Examples 9 to 11, Comparative Example 3

Production of a support

[0119] A 0.3-mm thick aluminum plate was washed with trichloroethylene to degrease. Then the surface of the aluminum plate was pebbled using a nylon brush and a 400 mesh pumice/water suspension and was then thoroughly washed with water. This plate was immersed in an aqueous 25% sodium hydroxide solution at 45°C for 9 seconds to carry out etching, followed by washing with water. The plate was further immersed in a 20% nitric acid solution for 20 seconds and then washed with water. At this time, the amount of etching of the pebbled surface was about 3 g/m². Next, the plate was formed with a 3 g/m² d.c. anodic oxidation film, using 7% sulfuric acid as an electrolyte at a current density of 15 A/dm². After that, the plate was washed with water and dried and further coated with the aforementioned undercoat solution 2. The film was dried at 90°C for one minute. The amount of the film applied was 10 mg/m² after drying.

[0120] The resulting support was coated with the following light-sensitive solution 11A and dried at 100°C for 2 minutes to form a layer (A). The amount to be applied was 1.3 g/m² after it was dried.

[0121] After that, the following light-sensitive solutions 11B to 14B were respectively applied and dried at 100°C for 2 minutes to form a layer (B) (upper layer) and obtain planographic printing master plates 11 to 14. The total amount of each light-sensitive solution after drying was 1.8 g/m². Among these planographic printing master plates, those using the light-sensitive solutions 11B to 13B using a xylene-containing novolac resin were designated as Examples 9 to 11 respectively. Also, a planographic printing master plate produced using the light-sensitive solution 10 containing a known novolac resin was designated as Comparative Example 3.

Light-sensitive solution 11A

[0122]

- Copolymer 1 0.75 g
- Cyanine dye A 0.04 g

- p-Toluenesulfonic acid 0.002 g
- Tetrahydrophthalic acid anhydride 0.05 g
- Dye in which the counter ion of Victoria Pure Blue BOH was 1-naphthalenesulfonic acid anion 0.015 g
- Fluorine type surfactant 0.02 g
- 5 (Product name: Megafac F-177, manufactured by Dainippon Ink and Chemicals)
- γ -butyrolactone 8 g
- Methyl ethyl ketone 7 g
- 1-Methoxy-2-propanol 7 g

10 Light-sensitive solutions 11B to 14B

[0123]

- Novolac resin (resin described in Table 4) 0.25 g
- 15 • Pyrylium dye B 0.05 g
- n-Dodecyl stearate 0.02 g
- Fluorine type surfactant 0.05 g
- (Product name: Megafac F-177, manufactured by Dainippon Ink and Chemicals)
- Methyl ethyl ketone 7 g
- 20 • 1-Methoxy-2-propanol 7 g

Table 4

25		Planographic printing plate	Light-sensitive solution	Novolac resin Novolac resin
	Example 9	Planographic printing plate 11	Light-sensitive solution 11	Novolac resin 2
30	Example 10	Planographic printing plate 12	Light-sensitive solution 12	Novolac resin 3
	Example 11	Planographic printing plate 13	Light-sensitive solution 13	Novolac resin 4
35	Comparative Example 3	Planographic printing plate 14	Light-sensitive solution 14	Novolac resin 6

Evaluation of planographic printing master plates

40 [0124] The resulting planographic printing master plates of Examples 6 to 11 and Comparative Examples 2 and 3 were stored and exposed with the same method as for Example 1 and developed by the following method to evaluate sensitivity and aging stability.

Developing treatment

45 [0125] 20 litres of an alkali developing process solution C (pH: about 13) or an alkali developing process solution D (pH: about 13.2) respectively having the following compositions was filled into a developing process vessel of a commercially available automatic developing machine LP-900H (manufactured by Fuji Photo Film Co., Ltd.) provided with a dipping-type developing vessel and kept at 30°C. 8 litres of tap water was laid in a second bath of the LP-900H and a finishing gum solution prepared by diluting FP-2W (manufactured by Fuji Photo Film Co., Ltd.) with water (1:1) was laid in a third bath of the LP-900H. The exposed planographic printing plates 7 to 14 were each developed in the automatic developing machine provided with a developing process solution suitable to the planographic printing plate. 50 The alkali developing process solutions used here and the results of evaluation are shown in Table 5 below.

Composition of the alkali developing process solution C

55 [0126]

- D sorbitol 2.5% by weight

- Sodium hydroxide 0.85% by weight
- Diethylenetriaminepenta (methylenephosphonic acid)5 Na salt 0.05% by weight
- 5 • Water 96.6% by weight

Composition of the alkali developing process solution D

[0127]

- 10 • D sorbitol 5.0% by weight
- Sodium hydroxide 1.7% by weight
- 15 • Diethylenetriaminepenta (methylenephosphonic acid)5 Na salt 0.1% by weight
- Water 93.2% by weight

Table 5

	Clear sensitivity (mJ/cm ²)			
	Alkali developing process solution C		Alkali developing process solution D	
	Ambient temperature aging	45°C, 75% humidity aging	Ambient temperature aging	45°C, 75% humidity aging
25 Example 6	56	61	-	-
Example 7	-	-	56	61
Example 8	51	61	-	-
30 Comparative Example 2	72	122	-	-
Example 9	56	61	-	-
Example 10	-	-	61	67
35 Example 11	51	56	-	-
Comparative Example 3	79	145	-	-

40 [0128] As is clear from Table 5, the planographic printing master plate according to the present invention had high sensitivity and excellent stability over time. On the other hand, the Comparative Examples, provided with light-sensitive layers having the same structure as the Examples except that conventionally known novolac resin was used, had insufficient storage stability.

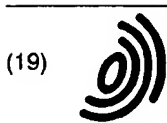
45 [0129] The planographic printing master plate of the present invention produces effects of high sensitivity, limited reduction in sensitivity over time and high stability with time.

Claims

- 50 1. A positive planographic printing plate comprising a support and a light-sensitive layer formed on the support, the light-sensitive layer including a light-sensitive image-forming material comprising a novolac resin that includes a xylenol monomer and a material that absorbs light and generates heat.
- 55 2. A positive planographic printing plate according to Claim 1, wherein the novolac resin is selected from the group consisting of 3,5-xylenol, 2,3-xylenol, 2,5-xylenol and 3,4-xylenol.
- 3. A positive planographic printing plate according to Claim 1, wherein the novolac resin has a weight average mo-

molecular weight of from 500 to 10,000.

4. A positive planographic printing plate according to Claim 1, wherein the light-sensitive layer includes alkali-soluble resin, the alkali-soluble resin comprises the novolac resin, and, if a percent by weight proportion of the novolac resin in the alkali-soluble resin is Y% by weight and content of the xylenol monomer in the novolac resin is X% by weight, then $X \times Y \geq 500$.
5. A positive planographic printing plate according to Claim 1, wherein the novolac resin comprises 20 to 90% by weight of total solids of the light-sensitive image-forming material included in the light-sensitive layer.
6. A light-sensitive image-forming material comprising a xylenol monomer-containing novolac resin and a material which absorbs light and generates heat.
7. A light-sensitive image-forming material according to Claim 6, wherein the novolac resin is selected from the group consisting of 3,5-xylenol, 2,3-xylenol, 2,5-xylenol and 3,4-xylenol.
8. A light-sensitive image-forming material according to Claim 6, wherein the xylenol monomer-containing novolac resin has a weight average molecular weight of from 500 to 10,000.
9. A light-sensitive image-forming material according to Claim 6, wherein the material includes alkali-soluble resin, the alkali-soluble resin comprises the xylenol monomer-containing novolac resin, and, if a percent by weight proportion of the xylenol monomer-containing novolac resin in the alkali-soluble resin is Y% by weight and content of the xylenol monomer in the xylenol monomer-containing novolac resin is X% by weight, then $X \times Y \geq 500$.
10. A light-sensitive image-forming material according to Claim 6, wherein the xylenol monomer-containing novolac resin comprises 20 to 90% by weight of total solids of the light-sensitive image-forming material.



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(71) Applicant: **Fuji Photo Film Co., Ltd.**
Kanagawa-ken (JP)

(54) Planographic printing plate precursor

(57) A positive planographic printing plate which has high sensitivity, limited reduction in sensitivity over time and high stability over time. The positive planographic printing plate has a light-sensitive layer formed on a support. The light-sensitive layer includes a light-sensitive image-forming material and a material which absorbs light and generates heat. The light-sensitive image-

forming material contains a novolac resin having a xylenol monomer. It is preferable that, if a proportion of the xylenol-containing novolac resin in alkali-soluble resin that forms the light-sensitive layer is Y% by weight and a content of the xylenol monomer in the novolac resin is X% by weight, $X \times Y$ is 500 or more ($X \times Y \geq 500$).

EP 1 162 063 A3

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EP 01 11 2912

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	EP 0 943 451 A (AGFA GEVAERT NV) 22 September 1999 (1999-09-22) * examples 2,3 *	1-10	G03F7/42 B41C1/10 C08L61/06 G03F7/023
X	EP 0 890 879 A (AGFA GEVAERT AG) 13 January 1999 (1999-01-13) * page 6, line 10 - line 36 *	1,2,6,7	
X	EP 0 900 653 A (AGFA GEVAERT AG) 10 March 1999 (1999-03-10) * examples *	1-10	
X	EP 0 950 513 A (AGFA GEVAERT NV) 20 October 1999 (1999-10-20) * paragraphs '0029!', '0030!', '0083!', '0088!' *	1,2,6,7	
X	EP 0 950 517 A (AGFA GEVAERT NV) 20 October 1999 (1999-10-20) * paragraphs '0030!', '0031!', '0064!' *	1,2,6,7	
X	WO 00 29214 A (MITSUBISHI CHEM CORP) 25 May 2000 (2000-05-25) * page 30, line 14 - page 31, line 12 * * page 8, line 10 - page 30, line 13 *	1-3,6-8	TECHNICAL FIELDS SEARCHED (Int.Cl.7) B41C C08L G03F
X	EP 0 978 376 A (AGFA GEVAERT AG) 9 February 2000 (2000-02-09) * paragraph '0020!'; claim 6 * * claims *	1,2,6,7	
D,X	EP 0 823 327 A (MITSUBISHI CHEM CORP) 11 February 1998 (1998-02-11) * page 21, line 36 - page 22, line 3; claim 1 *	1-3,6-8	
		-/--	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 9 September 2003	Examiner Heywood, C
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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Application Number
EP 01 11 2912

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
E	US 2002/058207 A1 (HINO ETSUKO ET AL) 16 May 2002 (2002-05-16) * paragraph '0039! - paragraph '0041!; claims *	1-3,5-8, 10	
X	& JP 2000 056470 A (MITSUBISHI CHEM CORP) 25 February 2000 (2000-02-25)	1-3,5-8, 10	
X	EP 0 934 822 A (MITSUBISHI CHEM CORP) 11 August 1999 (1999-08-11) * paragraphs '0028!, '0031!, '0032!, '0034! *	1-3,5-8, 10	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 9 September 2003	Examiner Heywood, C
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EPO FORM 1503 03/02 (P04001)

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0943451	A	22-09-1999	EP 0943451 A1	22-09-1999
			DE 69901642 D1	11-07-2002
			DE 69901642 T2	30-01-2003
			JP 2000035662 A	02-02-2000
			US 6153353 A	28-11-2000
EP 0890879	A	13-01-1999	DE 19729067 A1	14-01-1999
			DE 59806683 D1	30-01-2003
			EP 0890879 A2	13-01-1999
			JP 11072919 A	16-03-1999
			US 2002061460 A1	23-05-2002
EP 0900653	A	10-03-1999	DE 19739302 A1	11-03-1999
			DE 59803175 D1	04-04-2002
			EP 0900653 A1	10-03-1999
			JP 11147378 A	02-06-1999
			US 2002009671 A1	24-01-2002
EP 0950513	A	20-10-1999	EP 0950513 A1	20-10-1999
			DE 69802374 D1	13-12-2001
			DE 69802374 T2	25-07-2002
			JP 2000056448 A	25-02-2000
			US 2001001699 A1	24-05-2001
EP 0950517	A	20-10-1999	EP 0950517 A1	20-10-1999
			DE 69900322 D1	08-11-2001
			DE 69900322 T2	04-07-2002
			JP 2000131832 A	12-05-2000
			US 2001001701 A1	24-05-2001
WO 0029214	A	25-05-2000	AT 236791 T	15-04-2003
			AU 757494 B2	20-02-2003
			AU 1179900 A	05-06-2000
			BR 9915407 A	24-07-2001
			CA 2349307 A1	25-05-2000
			CN 1331632 T	16-01-2002
			DE 69906818 D1	15-05-2003
			EP 1159133 A1	05-12-2001
			WO 0029214 A1	25-05-2000
			JP 2001133965 A	18-05-2001
			NO 20012388 A	16-07-2001
			US 6596457 B1	22-07-2003
EP 0978376	A	09-02-2000	DE 19834746 A1	03-02-2000
			EP 0978376 A2	09-02-2000
			JP 2000206687 A	28-07-2000

EPO FORM P0459

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**ANNEX TO THE EUROPEAN SEARCH REPORT
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09-09-2003

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0978376 A.		US 2002006575 A1	17-01-2002
EP 0823327 A	11-02-1998	EP 0823327 A2	11-02-1998
		JP 10268512 A	09-10-1998
		JP 2002365792 A	18-12-2002
		US 6410207 B1	25-06-2002
		US 6326122 B1	04-12-2001
		US 2002146635 A1	10-10-2002
US 2002058207 A1	16-05-2002	JP 2000056470 A	25-02-2000
		JP 11327163 A	26-11-1999
EP 0934822 A	11-08-1999	EP 0934822 A1	11-08-1999
		JP 11288089 A	19-10-1999
		US 6200727 B1	13-03-2001

EPO FORM P459

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